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Spectrophotometric Determination of Average Concentration of Sulfur-Dioxide in Air by Permeation Through Polymer Membranes.

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SPECTROPHOTOMETRIC DETERMINATION OF AVERAGE CONCENTRATION OF SULFUR DIOXIDE IN AIR BY PERMEATION THROUGH POLYMER MEMBRANES

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To Jane

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ABSTRACT

The importance of the determination of the average concentration of sulfur dioxide in air has been demonstrated by the Federal regulations stipulating that the average daily concentration must not exceed 365 $\mu g/m^3$ for more than one day during a year and the average concentration for that year must not exceed 80 $\mu g/m^3$. The methods commonly used for monitoring the average concentration are based on the use of various automatic monitors or the use of lead peroxide candle or sulfation plate methods. Automatic or continuous monitors are expensive and an average concentration can be obtained from them only with time-consuming and expensive efforts. The lead candle method, although less expensive, lacks sensitivity and specificity and involves complex analytical techniques. Therefore a definite need exists for a simple and sensitive technique for measuring the average concentration of sulfur dioxide.

A new method is now proposed which is simple, low in cost, essentially free of interferences and may be employed for sampling times as short as one day. Of special significance is the fact that this new method provides "integrated" values directly - average concentrations are provided for each selected exposure period and therefore relate directly to Federal or State standards.

This method consists of a very simple sampling procedure coupled with the West-Gaeke procedure for subsequent determination of the trapped sulfur dioxide. For the analysis of air, a glass tube covered on one end with a silicone rubber membrane and stoppered on the other end, is

filled with a solution of 1.0 M sodium tetrachloromercurate (II). When the tube is exposed to air containing sulfur dioxide, the sulfur dioxide permeates through the membrane and is absorbed by the sodium tetrachloromercurate (II) solution. After the solution in the tube is returned to the laboratory, it may be analyzed by the West-Gaeke method by adding the color-developing solutions of formaldehyde and acid-bleached pararosaniline and measuring the absorbance at 575 nm. With an 11 cm^2 membrane exposed for 1 day, a detection limit of 10 $\mu g/m^3$ can be projected.

CHAPTER I

INTRODUCTION

"And God said, Let us make man in our image, after our likeness: and let them have dominion over the fish of the sea, and over the fowl of the air, and over the cattle, and over all the earth, and over every creeping thing that creepeth upon the earth" (Genesis 1:26). And so it is, technological advances have given man dominion over the earth and even the very power to destroy it.

Such terms as environment, ecology and pollution are common to our time. If man does not learn to control the use of the technology that he has developed he may eventually effect self annihilation. In this time of trial a new technology must be developed to monitor and control existing technologies so that people can live without fear that the air which they breathe, the water which they drink and the food which they eat will endanger them.

Sulfur dioxide is probably the most widely known and uniformly distributed of the important air pollutants. This dissertation describes a new technique for monitoring the average concentration of sulfur dioxide in air. It is hoped that it will aid in man's quest for a healthy environment.

A. SOURCES OF SULFUR DIOXIDE

Sulfur dioxide is introduced into the atmosphere through natural as well as man made sources. While the only apparent natural source is that of volcanic gases, many of man's activities result in sulfur diox-

ide emissions. The total annual world emission of sulfur dioxide was estimated to be 146 million tons in 1965 (1). The emission of sulfur dioxide over the United States in 1966 was 28.6 million tons (2). Of this total 58% and 19% were emitted from the combustion of coal and fuel oil, respectively, and 12% comes from the smelting of ores. Other sources of sulfur dioxide were oil refining operations (5.5%), coke processing (1.8%), sulfuric acid manufacture (1.9%), coal refuse banks (1.4%) and refuse incineration (0.4%). It is interesting to note that 46% of all sulfur dioxide in the United States is emitted in the operation of electrical power generating facilities (3). It is obvious that these figures could have changed somewhat over the last six years due to changes in the use of pollution abatement equipment; however, they should give a general picture of the extent of sulfur dioxide emissions.

B. THE IMPORTANCE OF SULFUR DIOXIDE

The importance of sulfur dioxide as an atmospheric pollutant is threefold. First sulfur dioxide is a pollutant in its own right since it is harmful to plants, animals, including man, and materials of construction. It may also act synergistically with other pollutant species, especially particulate matter, to cause harmful effects. Secondly, it can play a significant role in photochemical smog formation and thirdly, it inevitably is oxidized to form sulfuric acid aerosol or sulfate and can, to some extent, be used as an indicator or precursor to sulfuric acid aerosol concentration.

Sulfur dioxide pollution has been associated with several tragic

disasters including Meuse Valley, Belgium in 1950, Donora, Pennsylvania in 1948, and London in 1952, as well as several other episodes that have occurred since then in London, Rotterdam, Japan and the eastern parts of the United States (6). Approximately 4,000 deaths were associated with the 1952 London disaster where the maximum daily average sulfur dioxide concentration reached a value of 4,000 $\mu g/m^3$ (1.5 ppm). The method used for determining this concentration, however, would not have distinguished between sulfur dioxide and sulfuric acid aerosol. Little data were obtained concerning other pollutant species; so, definite conclusions about the role of sulfur dioxide could not be made. There is little doubt, however, that sulfur dioxide directly or indirectly had an effect on the increased death rate. Post-mortems carried out on some of the victims indicated that they had previous histories of respiratory or cardiovascular ailments.

There has been a great deal of work done on the short-term effects of high concentrations of sulfur dioxide on humans and animals (1, 7). However, little laboratory work has been done with lower concentrations commonly encountered in the ambient atmosphere. The odor threshold for man is generally considered to be between 1300 $\mu g/m^3$ (0.50 ppm) and 5,000 $\mu g/m^3$ (1.9 ppm) (2) while bronchoconstriction occurs at 15,000 $\mu g/m^3$ (5.7 ppm) for a 1 hour exposure for a sensitive human subject, and severe distress occurs when he is exposed to 30,000 $\mu g/m^3$ (79 ppm) for 1 hour. These studies can still be of some value when it is considered that most sources of sulfur dioxide are point sources and very high concentration short term exposures may occur even though the

average concentration may be relatively low.

Epidemiological studies, on the other hand, give an indication that much lower concentrations may even be a health hazard (1). It must be understood that sulfur dioxide is not the only pollutant species present in ambient atmospheres; therefore, conclusions from epidemiological studies may be somewhat misleading. Other pollutants present may also cause this effect or alternatively synergistic interaction of other species with sulfur dioxide may result in such a health hazard. Studies indicate that sulfur dioxide concentrations as low as 120 $\mu g/m^3$ (0.046 ppm, annual mean) result in increased frequency and severity of respiratory diseases. When the concentration of this pollutant goes to 300 $\mu g/m^3$ (0.11 ppm, 24 hour mean) with low smoke levels, increased hospital admissions have been reported; however, if the concentration is increased to 500 $\mu g/m^3$ (0.19 ppm, 24 hour mean) with low particulate levels, higher mortality has been observed.

The effect on vegetation and materials of construction can also be quite dramatic. Concentrations as low as 345 $\mu g/m^3$ (0.13 ppm) may cause adverse effects on materials of construction, and levels of about 85 $\mu g/m^3$ (0.03 ppm, annual mean of sulfur dioxide may cause chronic plant injury and excessive leaf drop. It is interesting to note at this point that the new Federal standards for sulfur dioxide in the ambient atmosphere correlate well with the lowest sulfur dioxide concentration at which harmful effects have been shown to occur. The present standards require that the annual arithmetic mean not ex-

ceed 80 $\mu g/m^3$ (0.03 ppm) and the maximum average concentration for any 24 hour period not exceed 365 $\mu g/m^3$ (0.14 ppm) for more than one day per year.

C. PRESENT METHODS FOR DETERMINING AVERAGE CONCENTRATION OF SULFUR DIOXIDE

A literature survey reveals that the average concentration of sulfur dioxide may be determined by continuous monitoring, sequential sampling and lead peroxide sulfation methods. Continuous monitoring methods have been based on conductometric, spetrophotometric, coulometric, infrared and flame photometric methods of analysis (32). Most of these methods are fairly sensitive; however, the conductometric and flame photometric methods lack specificity. They all are costly. A typical instrument with recorder costs $5,000.00 which amounts to a capital outlay of $50,000.00 for a small sampling network of ten stations. Telemetering facilities add thousands of dollars to the cost of operation. It is also expensive and time-consuming to convert the primary data obtained from these instruments to an average concentration.

Sequential samples are commonly taken by pulling air through an absorbing solution for a 24 hour period. The West-Gaeke (10) sampling and analysis scheme is probably the best system to use when taking sequential samples. Although the method is very sensitive and selective, maintaining constant sample flow rates for long periods of time is somewhat difficult. As with continuous monitors, sequential samplers usually require 110 volts AC electrical power. An average price for

such a sampler is $800.00.

The lead peroxide sulfation methods which are in common use at present will be discussed in detail here since they are "effects methods" and are comparable to the method developed here. The lead candle (11) is made by placing a paste consisting of lead dioxide, water, ethanol, and gum tragonanth on the surface of a glass jar that has been covered with cotton gauze. The cylinder or candle as it is sometimes called is allowed to dry and is stored in air that is free of sulfur dioxide. The candle is then exposed to ambient air in an enclosure that protects the reactive surface from rain, but allows air to circulate in and out freely. Sulfation plates (12) are made simply by coating the lead dioxide paste on the inside of a petri dish. While being exposed to the ambient atmosphere, the plate is inverted to protect the reactive surface from rain. Sulfur dioxide reacts with the lead dioxide of the plate or candle to yield lead sulfate. Sulfate is then determined gravimetrically as barium sulfate (11), turbidimetrically (12) or spectrophotometrically (13). The first two procedures require dissolution and the last one requires combustion of the sample.

Although the lead candle and sulfation plate methods are fairly inexpensive to use, they have many failings. The rate at which sulfation takes place has been found to be proportional to sulfur dioxide concentration; however, it is also dependent upon wind velocity, humidity and temperature (14). The methods also suffer from the necessity of precise and uniform preparation of the candle or plate, extended sampling periods and time-consuming analytical operations as described

above. Sampling periods vary from one to several months. Furthermore, sulfation is inherently nonspecific since other sulfur compounds that react with lead dioxide may cause formation of sulfate in addition to that resulting from sulfur dioxide exposure. For example, much higher results than would be expected from sulfur dioxide exposure alone have been found when hydrogen sulfide is present (33, 34).

The main reason that the 37 year old lead candle method has not been relegated to obsolesence is due to the fact that there is no suitable alternative method. The method is able to give only approximate data that indicates the total insult to the environment for a long period of time. Therefore, a serious need exists for a method for determining average concentration of sulfur dioxide with increased sensitivity, specificity and ease of sample analysis. It was a prime objective to develop a method that could be used to determine the average concentration for a twenty four hour period at the low levels that the Federal standards require.

D. DEVELOPMENT OF PRESENT METHOD

There were several approaches that were considered in the development of this method. Since the West-Gaeke Method (10) is considered throughout the world to be the reference method for determining sulfur dioxide in air, it was thought that this would be an appropriate starting place for the development of a new method. The basic idea consisted of using the West-Gaeke approach of absorbing and stabilizing sulfur dioxide in sodium tetrachloromercurate (II) solution with some means for allowing the sulfur dioxide to be absorbed at a rate proportional

to concentration. Using a gel or gum as in the lead candle was immediately ruled out since a device so designed would be subject to many of the same problems which are associated with the lead candle method and would be mechanically difficult to design. The second approach was to make linear diffusion the rate-determining step. Experiments were undertaken, but diffusion was found to be a slow process (16) and absorption on the walls of the materials used in the diffusion apparatus occurred. The experiments which dealt with diffusion will not be covered in this dissertation. The third approach to controlling the rate of absorption of sulfur dioxide considered was to place a permeable polymer film between the absorbing solution and the air to be analyzed. The rate of permeation should be proportional to concentration. Permeation through the film or membrane is a function of the thickness and area of the film, type of film, temperature, humidity and concentration difference across the membrane. Since film thickness area and type can be held constant, the main effects to be measured when studying various types of membranes are the effect of temperature, concentration difference and humidity on the permeation rate. Temperature has a most dramatic effect on permeability in most cases; however, in the case of the diffusion of water vapor through polystyrene (17) and carbon dioxide through silicone rubber (18), temperature has little effect on permeability. It was therefore desirable to find a membrane that was highly permeable to sulfur dioxide and that had a low temperture effect. It was found that "Iolon", polyethylene, and the silicone rubber films had useful permeabilities, but only the permeabilities of

the silicone rubber films were relatively independent of temperature. At first it was thought that the form of the final device should be a sealed bag containing the absorbing solution. This would have allowed exposure of a large area of membrane and would have made a very convenient disposable device; however, this was not necessary due to the very high permeability of the silicone rubber films used. The sulfur dioxide measuring device consisted basically of a tube with a silicone rubber membrane sealed over one end of it. The sodium tetrachloromercurate (II) solution was placed inside the tube. After exposure, the sulfur dioxide in this absorbing solution was analyzed by the West-Gaeke procedure (10) by adding the color developing solutions of formaldehyde and p-rosaniline and reading the absorbance at 575 nm. It was found that the permeability of the membranes was not only relatively temperature independent but also independent of humidity. A detection limit of about 10 $\mu g/m^3$ (0.004) can be expected with a membrane area of 11 cm^2 and an exposure period of one day. This satisfies the Federal requirement that methods for determining sulfur dioxide must be sensitive to 25 $\mu g/m^3$ (0.01 ppm).

CHAPTER II

EXPERIMENTAL

A. APPARATUS

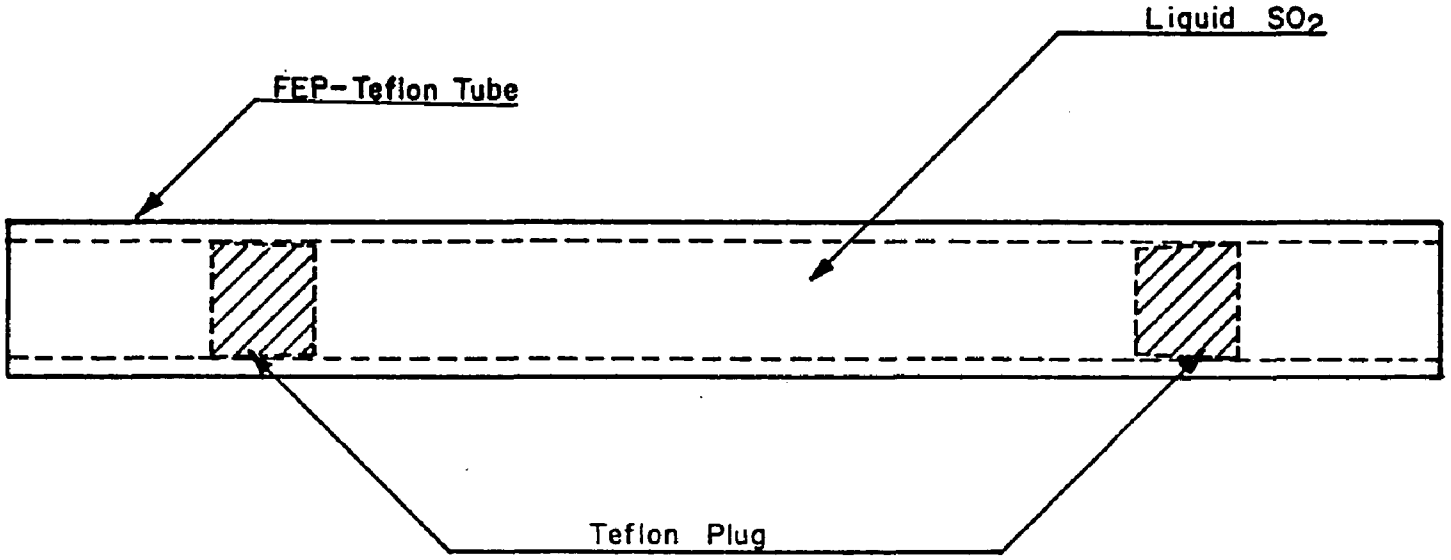
1. Basic Design of Sulfur Dioxide Exposure Apparatus. The apparatus used in these experiments consisted of two basic systems. First, the sulfur dioxide-air mixture preparation assembly cleaned and dried air from the laboratory and mixed it with sulfur dioxide being released by a permeation tube. Secondly, the permeation cell assembly was used to measure the permeability of various membranes to sulfur dioxide. Two types of permeability assemblies were used. One was for exposure of large areas of about 60 cm^2 of membrane material and the other was used for exposing small areas of 2 to 11 cm^2 of membrane.

2. Preparation and Use of Permeation Tubes. The permeation tube (Fig. 1) is a device developed by O'Keeffe and Ortman (19) which will emit a gas at a constant rate. It consists of a tube of FEP Teflon* (tetrafluoroethylene co hexafluoropropylene) normally 1/4 inch in diameter filled with liquid sulfur dioxide or other liquid and stoppered on both ends. The tubes prepared in this laboratory were made by first stoppering one end of a 1/4 inch O.D. FEP Teflon tube with a short piece of TFE Teflon* rod and then attaching the other end of the tube to a cylinder of sulfur dioxide. The tube was then filled with liquid sulfur dioxide, cooled with dry ice, released from the sulfur dioxide cylinder, allowed to warm until the liquid sulfur dioxide started to boil and stoppered on the open end with a second piece

*Registered Dupont Trademark

FIGURE 1

SULFUR DIOXIDE PERMEATION TUBE


Liquid SO_2
FEP-Teflon Tube
Teflon Plug

of Teflon rod. The tubes were stored in a desiccator until needed.

The sulfur dioxide inside the tube permeates through the tube wall and is emitted into the surrounding air at a rate highly dependent on the temperature of the tube. Therefore, this temperature must be controlled precisely, preferably to ± 0.1 °C or better. To accomplish this, a constant temperature bath that could be maintained at 30 ± 0.05 °C for a long period of time was used. The permeation tube was calibrated gravimetrically by weighing the tube several times over a one to two week period. Periodic weighings were made thereafter to ensure that constant permeation was occurring. Table I shows the permeation rate during the life of a typical permeation tube. The average permeation rate was about 5.25 µg/minute and remained almost constant during the life of the tube. Only a drop or two of liquid sulfur dioxide remained after 100 days. The deviation from 5.25 µg per minute for short time periods was probably due to inaccurate measurement of the small weight losses encountered here.

The hydrogen sulfide and nitrogen dioxide permeation tubes were obtained from Metronics Associates, Inc., Palo Alto, California.

3. Sulfur Dioxide -Air Mixture Preparation. The sulfur dioxide-air mixture was prepared by running a known amount of dry, uncontaminated air over the permeation tube (Fig. 2). Air from the laboratory was pumped by pump A through activated charcoal B, silica gel C and D, flowmeter E, condenser F, over the permeation tube H and finally, to one of the assemblies for measuring the permeability of various membranes. The purpose of the activated charcoal column was to remove

TABLE I

CALIBRATION OF PERMEATION TUBE

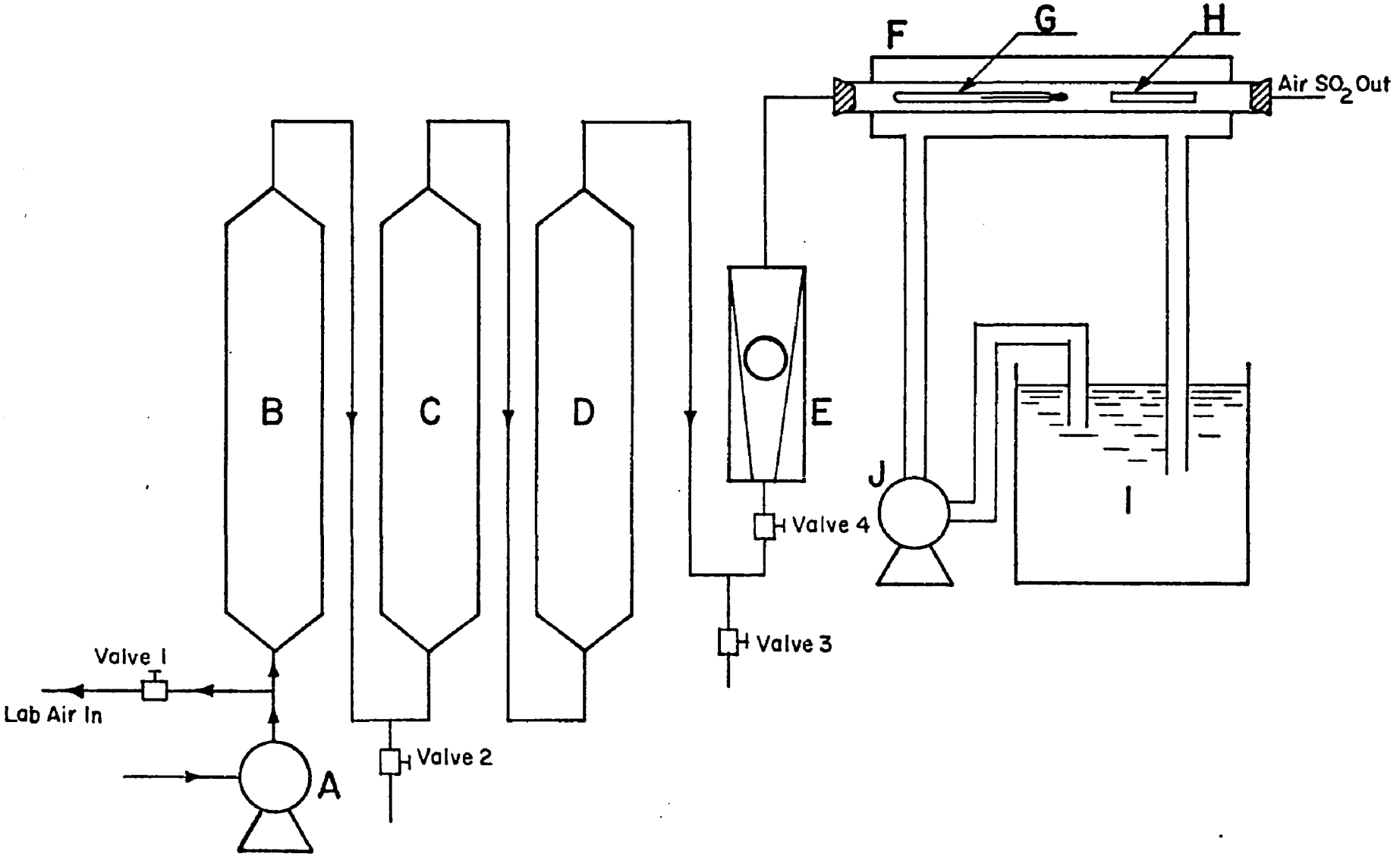
Time* (Days)	Time Between Weight Measurements (Days)	Permeation Rate (µg/min.)
1	1	5.27
2	1	4.98
3	1	5.45
5	2	5.23
6	1	5.52
7	1	4.85
10	3	5.25
12	2	5.17
12	12	5.25**
14	2	5.27
16	2	5.39
20	4	5.32
24	4	5.24
29	2	5.28
40	11	5.28
75	35	5.16
98	6	5.23
100	2	5.15

*This was the total time the permeation tube had been used.

**This value was calculated from the weight loss over the first 12 days the tube was weighed.

FIGURE 2

SULFUR DIOXIDE-AIR MIXTURE PREPARATION APPARATUS


F
G
H
Air SO_2 Out
B
C
D
E
J
I
Valve 4
Valve 3
Valve 1
Lab Air In
Valve 2
A

vapors, including sulfur dioxide, that were sometimes present in the laboratory. The silica gel columns were used to dry the air.

Drying the air serves a dual function. First the permeation tube must be in a dry atmosphere for gravimetric calibration (20). Water may be absorbed by the Teflon or the liquid sulfur dioxide inside the tube causing the weight of the tube to vary with humidity. Also the tube may be used in studies while it is being calibrated. Secondly, by using dry air, varying humidity could not affect the permeability of the membranes under investigation.

The permeation tube was kept in a condenser through which water was pumped from a water bath held at 30 ± .05 °C. A thermometer G was also placed in the condenser to monitor the temperature. The circulation pump J was located on the return line to the water bath to eliminate warming the water to the condenser.

4. Auxiliary Constant Temperature Baths. Auxiliary water baths used for keeping sulfur dioxide detection devices at constant temperatures were maintained to ± 0.05 °C; although the actual temperatures of permeation devices were probably not maintained to better than 0.5 °C. This is because the sulfur dioxide detection arrangements in general were well insulated.

5. Thermometers. All thermometers were correlated with an uncalibrated National Bureau of Standards thermometer which could be read to ± 0.01 °C. All other thermometers could be read to ± 0.05 °C or better.

6. Flowmeters. Rotameters were used throughout. They could mea-

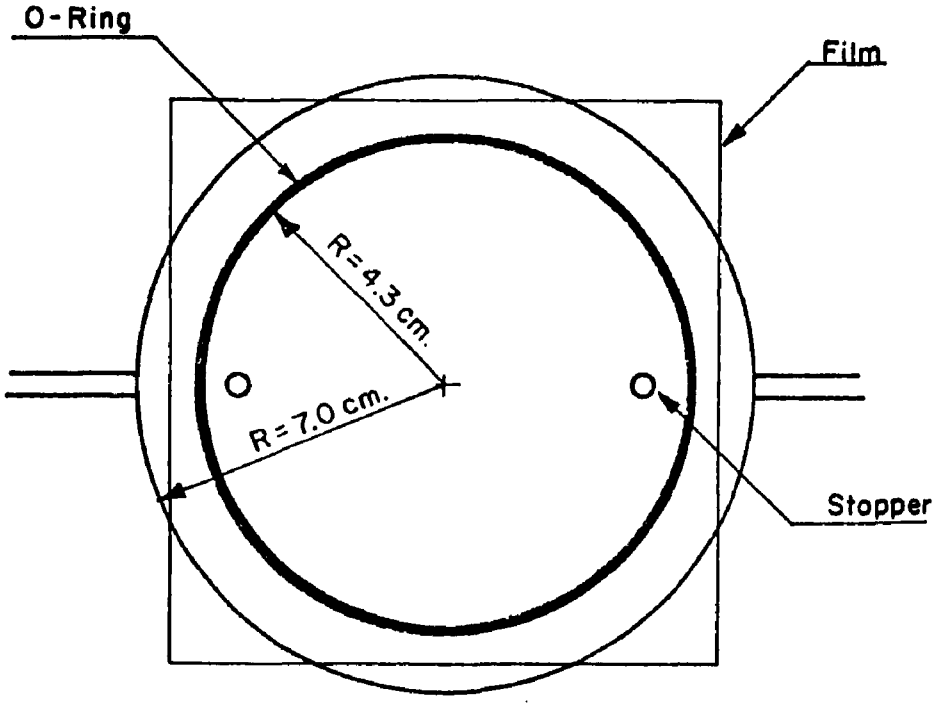
sure air flow reproducibly to ± 2% at full scale. Deviations of the pressure in the air distribution and sulfur dioxide preparation systems were kept to a minimum to eliminate effects of pressure on the rotameters.

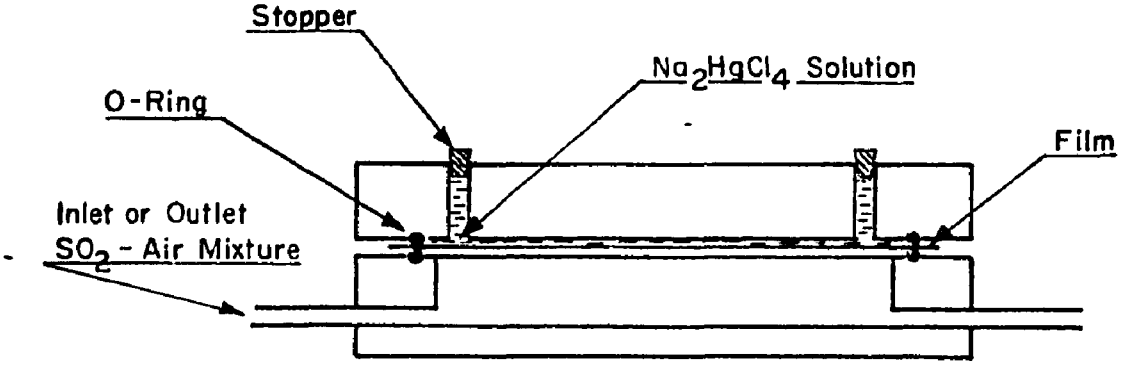
7. Cell Assembly for Preliminary Work. The cell assembly shown in Figure 3 was used for preliminary work to determine the permeabilities of many types of membranes. It allowed a large surface area to be exposed so that reasonable time periods and relatively low concentrations of sulfur dioxide could be used. This apparatus also solved the problem of sealing the membranes to some other article or to themselves. For instance, if bags were to be made out of the membranes, many different methods of sealing would be necessary for a study of the wide variety of films investigated here. In fact, TFE Teflon film could not be sealed by any readily available means. Therefore, O-rings were used to seal the membrane. This cell assembly, which was constructed of plexiglass, consisted of two compartments separated by the membrane under examination. On one side of the membrane was a solution of sodium tetrachloromercurate (II), on the other side was a known concentration of sulfur dioxide in air. This apparatus was, in effect, a concentration cell with the concentration of sulfur dioxide approximately zero on the solution side of the cell.

To fill the device with sodium tetrachloromercurate (II) solution a pipet filled with the solution was inserted into a hole in a plastic NMR tube stopper and the stopper with the pipet was inserted into one of the two holes on the top of the cell. Then the solution was

FIGURE 3

PERMEATION CELL ASSEMBLY FOR PRELIMINARY WORK


O-Ring
Film
R=4.3 cm.
R=7.0 cm.
Stopper

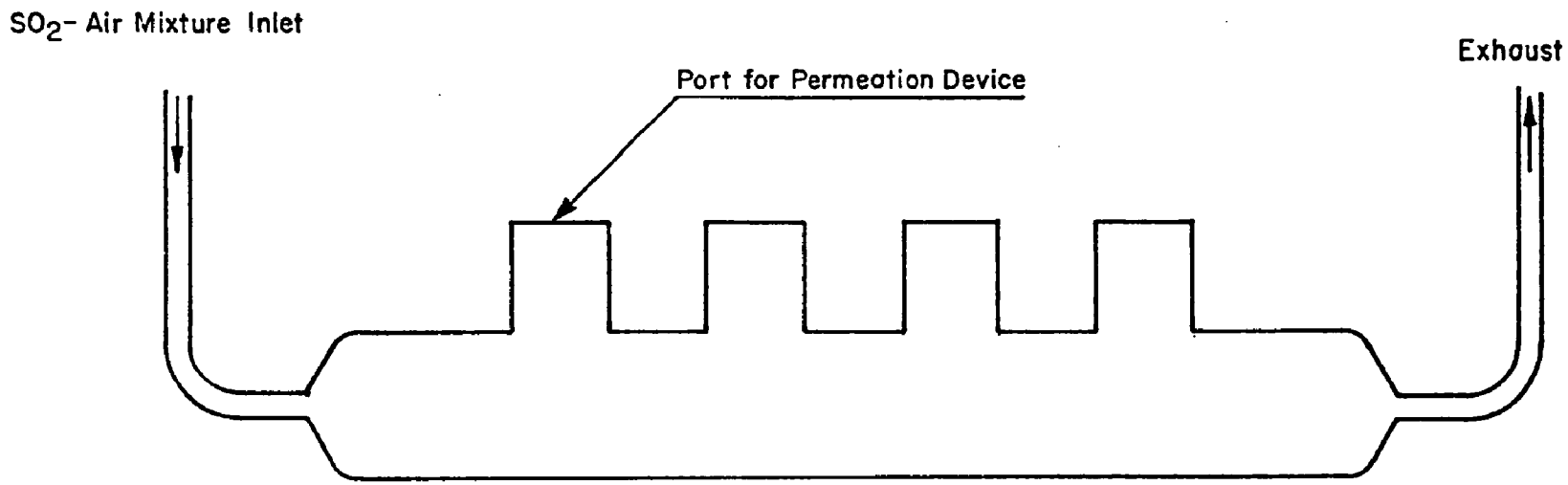

Stopper
Na_2HgCl_4 Solution
O-Ring
Film
Inlet or Outlet
SO_2 - Air Mixture

allowed to flow into the cell between the top plate and the membrane until it almost came out of the open hole. The cell was slanted during this operation so that the open hole was higher than the hole being filled. The open hole was then stoppered. If all of the solution in the pipet had not flowed into the cell, which was usually the case, it was sucked into the solution compartment by pulling a partial vacuum on the air side of the cell with a pipet bulb. After the solution compartment was just filled, a second stopper was placed in the filling hole. The entire operation was completed with as few bubbles as possible being admitted with the solution. Usually there were no bubbles in this compartment. The purpose of intimate contact between the film and the absorbing solution was to eliminate diffusion through a stagnant gas phase which might cause a decrease in the apparent permeation rate. Up to four of these devices were placed in water baths at the same time. Duplicate membrane samples were taken when enough material was available.

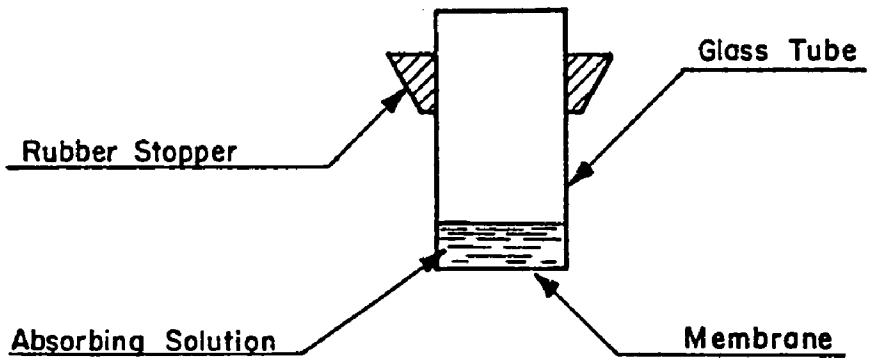
8. Exposure Chamber and Cell Assembly for Silicone Rubber Films. The exposure chamber shown in Figure 4 was used to expose the silicone rubber permeation devices to various concentrations of sulfur dioxide and various conditions and for calibration of the sulfur dioxide device. It consisted of a large tube through which the sulfur dioxide-air mixture was passed, and side tubes into which the permeation devices could be introduced. The tube of the permeation device was normally inserted into a one hole rubber stopper and the stopper was inserted into the exposure chamber to make an air tight seal. The entire apparatus could

FIGURE 4

EXPOSURE CHAMBER AND PERMEATION INSTRUMENT FOR SILICONE RUBBER STUDY



Exposure Chamber



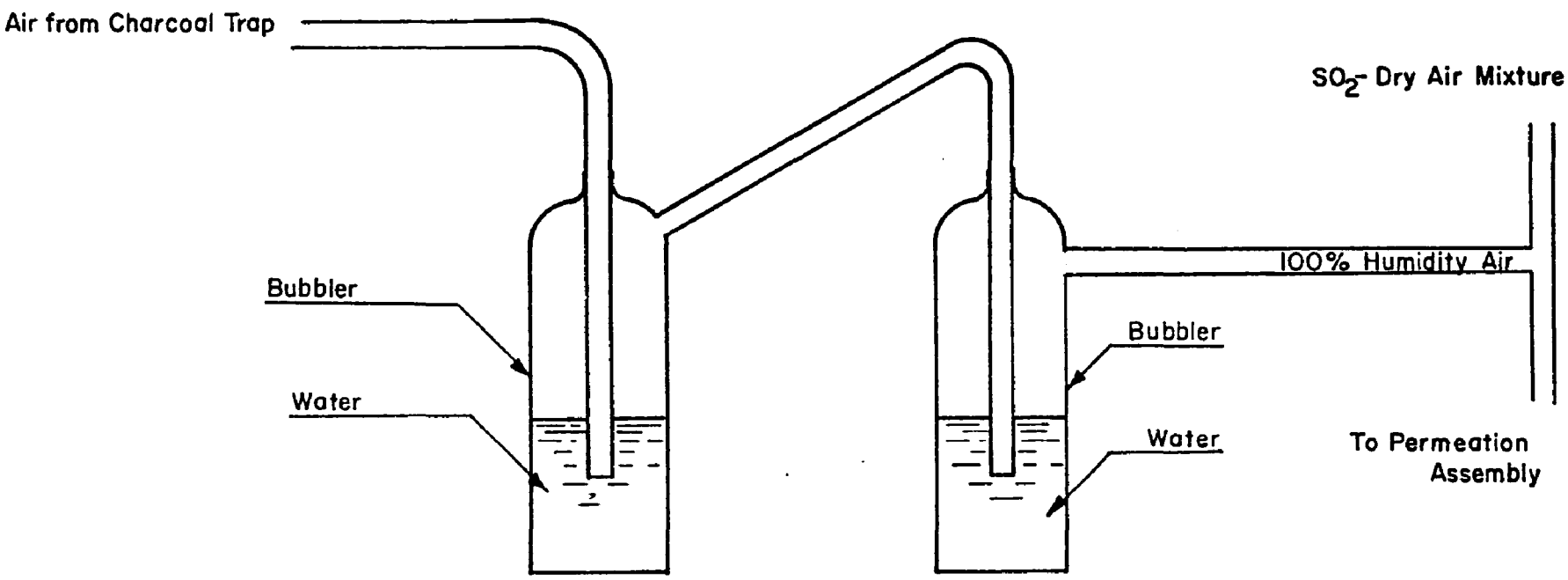
Permeation Device

then be submerged in a water bath. The silicone rubber membrane unit (Fig. 4) used to measure the permeability properties of this particular membrane was also used for the final form of the sulfur dioxide measuring device. It consisted simply of a glass tube covered on one end by the silicone rubber membrane. The membrane was sealed to the tube with silicone rubber cement. The tetrachloromercurate (II) solution which was placed in the permeation device was brought to the temperature of the bath that the exposure chamber was in so that no waiting period was needed to allow the permeation device to come to the bath temperature.

9. Humidity Experiments. The equipment shown in Figure 5 was used in the preparation of air-sulfur dioxide mixtures at the relative humidities of 0 and 80%. Dry air or air from the laboratory that had been scrubbed with the activated charcoal column in Figure 2 was passed through the two gas washing bottles at a flow rate of 800 ml/min. This flow was combined with 200 ml/minute of dry air-sulfur dioxide mixture that had been prepared with the permeation assembly in Figure 2. To prepare 0% relative humidity mixtures, no water was placed in the gas washing bottles and dry air was used. A relative humidity of 80% was prepared by passing air from the activated charcoal column through the bubblers with water in both bubblers. To insure saturation of the air passed through the bubblers, the first bubbler was warmed slightly so that condensation appeared at the top of the bubbler. The second bubbler remained at room temperature and no condensation was observed in it. Leaving the gas washing bottles in the circuit

FIGURE 5

EQUIPMENT FOR SATURATION OF AIR WITH WATER


Air from Charcoal Trap
SO_2- Dry Air Mixture
Bubbler
Water
100% Humidity Air
Bubbler
Water
To Permeation Assembly

for both relative humidity preparations eliminated geometry effects.

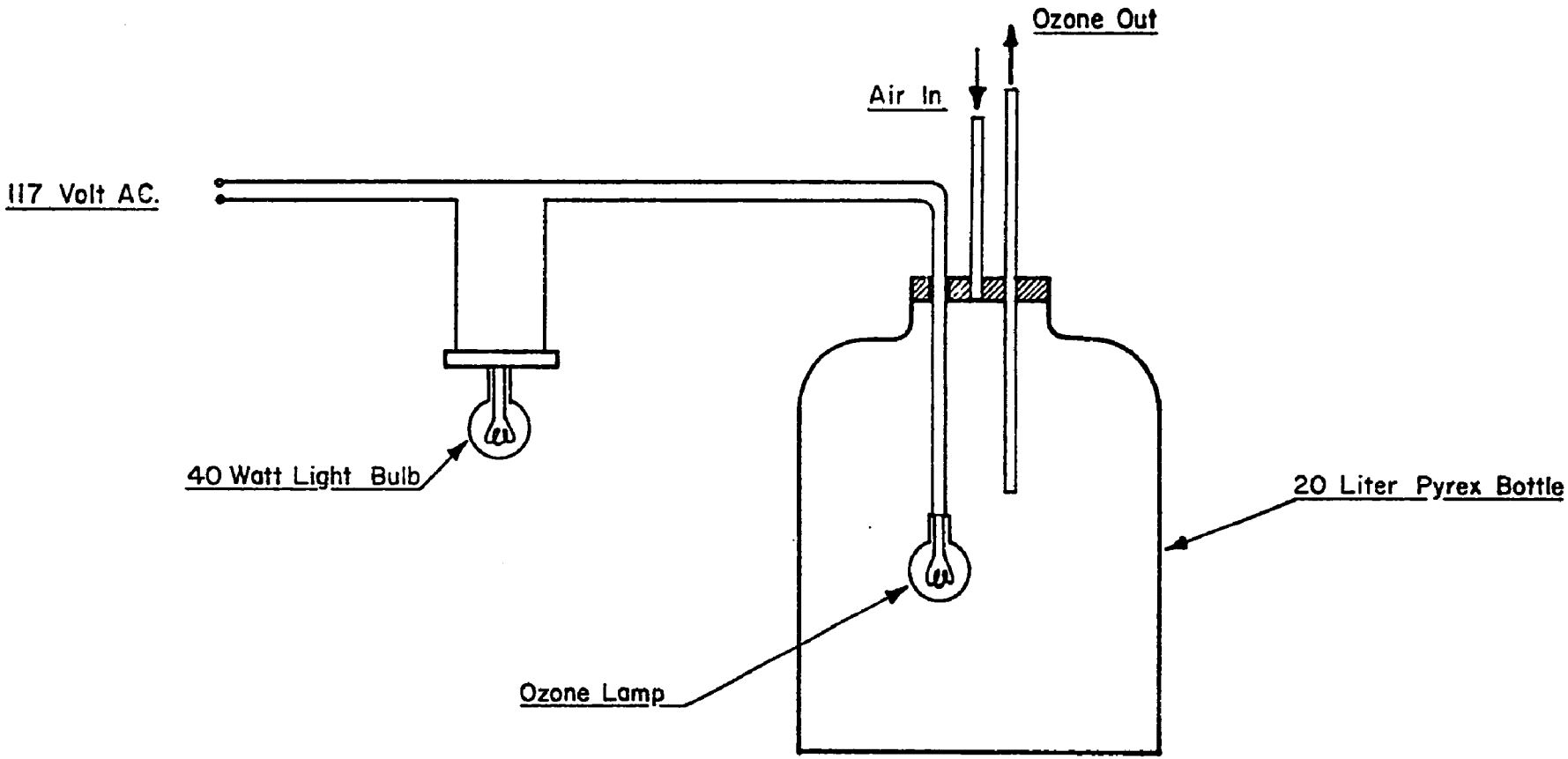
To simulate the formation of dew on the membranes, a third experiment was undertaken in which the sodium tetrachloromercurate absorbing solution was cooled to about 2°C. The tube was then placed in the exposure apparatus set up in the 80% relative humidity configuration. This caused condensation to form and remain on the tubes and membranes for about 1.5 hours of the five hour exposure period.

10. Interference Studies. The gas mixtures used in the interference studies were prepared in two ways. The hydrogen sulfide and nitrogen dioxide-air mixtures were prepared with permeation tubes in the same manner that the sulfur dioxide-air mixtures were prepared. The ozone-air mixture was prepared by flowing air through a twenty liter pyrex bottle. A mercury vapor germicidal lamp, (GE-OZ4S11) which was connected in series with a forty watt light bulb, was placed inside the bottle (Fig. 6). Ultraviolet light from the lamp produced ozone. The air from the ozone generator was mixed with fresh air to prepare the mixtures used here. The concentration of these mixtures was then monitored by a Frieze chemiluminescence ozone analyzer (Environmental Science Division, Bendix Corp.). Chemiluminescence is considered the reference method for determining ozone in air.

The interference studies were carried out in three different ways in order to simulate as closely as possible the effects of interfering species in the ambient atmosphere. The permeation instrument may be exposed to sulfur dioxide before, after or during exposure to interfering gases. The first situation was checked by introducing into the

FIGURE 6

OZONE PREPARATION EQUIPMENT


Ozone Out
Air In
117 Volt AC.
40 Watt Light Bulb
20 Liter Pyrex Bottle
Ozone Lamp

instrument a solution of sodium tetrachloromercurate (II) solution containing three concentrations of sulfur dioxide. The sulfur dioxide device was then exposed to the gas being examined for interfering effects. This was analogous to exposure to sulfur dioxide with subsequent exposure to an interfering gas. Secondly, the tube containing the absorbing solution without sulfur dioxide was exposed to the interferant-air mixture under investigation and then to sulfur dioxide for one hour. The last experiment was carried out by exposing the tubes to air containing sulfur dioxide and the species being examined for interference.

The first two experiments were carried out by simply using the interference mixtures described above; however, in the second of these experiments, with the exposure to sulfur dioxide, a set of indicator tubes were used to measure the concentration of sulfur dioxide and were exposed in a series arrangement with the tubes that had been exposed to the interfering gas-air mixture. In the last experiment several approaches were used to obtain the interference mixture. In all cases, a set of indicator tubes was exposed to the sulfur dioxide mixture. For hydrogen sulfide and ozone, a concentrated mixture of the interfering gas in air was mixed with this sulfur dioxide-air mixture. This interference mixture, which was diluted only slightly by the addition of the interfering gas, was used to expose a second set of tubes. In the case of nitrogen dioxide, the sulfur dioxide-air mixture that had traversed the indicator tube chamber was passed over the nitrogen dioxide permeation tube and then to the second

exposure assembly.

B. REAGENTS

1. Deionized Water. High quality deionized water was used in making up all reagents. The quality of the water is of utmost importance. It was found in this laboratory that chlorine was not removed in an all glass still even when the still was operated so that considerable amounts of steam were allowed to pass through the condenser. The concentration of chlorine in the distilled water by the o-tolidine estimation ran as high as 1.0 ppm (30). This caused a negative interference with the West-Gaeke method of about 3 µg of sulfur dioxide. However, this water was essentially free of metal contaminants and had been used successfully in research with trace metals for several years.

2. Sodium Tetrachloromercurate (II) Solutions. To make 1 M sodium tetrachloromercurate (II) solution, 1 mole (272 grams) of reagent grade mercuric chloride (Mallinkrodt Chemical Works) and 2 moles (117 grams) of sodium chloride (Mallinkrodt Chemical Works or Matheson Coleman and Bell) were dissolved in deionized water and diluted to one liter. From this solution 250 and 100 ml portions were individually diluted to one liter to make 0.4 and 0.1 M solutions. Since mercuric chloride is only sparingly soluble in water, either the sodium chloride must be dissolved first or the two materials must be dissolved simultaneously. It is interesting to note here that the potassium tetrachloromercurate (II) salt is less soluble than the sodium salt and that a 1 M solution of potassium tetrachloromercurate (II) is almost saturated making it difficult to prepare such solutions.

3. Pararosaniline Solution. This solution was supplied by Kem-Tech Laboratories, Inc., Baton Rouge, Louisiana, in a concentrated form. A recent preparation of this solution consists of dissolving 0.64 g pararosaniline hydrochloride (Fisher Scientic Co., No. P-389) in 240 ml of concentrated hydrochloric acid and diluting to 1 liter with water. Impure pararosaniline may result in high reagent blanks. Reagent blanks of 0.015 and 0.008 were obtained here for the 0.1 and 1 M sodium tetrachloromercurate (II) solutions, respectively. Twenty-five milliliters of the concentrate was diluted to 100 ml with water. This resulting solution is stable for at least three months. The concentrate is stable for at least a year.

4. Formaldehyde, 0.2%. To prepare this reagent 5 ml of 37% formaldehyde (Mallinkrodt Chemical Works) was diluted to 1 liter with deionized water. This solution was prepared daily.

5. Sulfamic Acid, 0.6%. Sulfamic acid (0.60 gram) was dissolved in deionized water and diluted to 100 ml. The reagent could be kept at room temperature for several days or in a refrigerator for two to three weeks.

C. PROCEDURES

1. Pretreatment of Samples. The preliminary studies were carried out without compensation for the water lost during the exposure to sulfur dioxide. Subsequent experiments, however, were carried out by pouring the absorbing solution into a 25 ml Erlenmeyer flask that had been previously weighed. Deionized water was then added until the ori-

ginal weight of the sodium tetrachloromercurate (II) solution had been regained. This sample was then subjected to analysis by the procedure described in the following section.

2. Procedure for Determination of Sulfur Dioxide. To the 10 ml sample, 1.0 ml each of the formaldehyde and pararosaniline solutions was added. The mixture was then allowed to stand for 30 minutes if the sodium tetrachloromercurate (II) solution was 0.1 M or 40 minutes if it was more concentrated. The absorbance versus a reagent blank was then read on a spectrophotometer at 560, 570 or 575 nm for 0.1, 0.4 or 1.0 M absorbing solutions respectively. If the sample had been exposed to ozone, it was allowed to stand for 30 minutes to permit the ozone to decompose. Some samples that were used in the nitrogen dioxide interference studies were treated with 1 ml of the sulfamic acid solution and allowed to stand 10 to 20 minutes prior to analysis. The use of this reagent is noted in the tables relating to this study.

CHAPTER III

RESULTS AND DISCUSSION

A. THEORY OF PERMEATION

Since this dissertation is mainly concerned with permeation, a brief review of this phenomenon will be given here. Transport of gases through solids may occur simply by diffusion through the pores of the membrane material, by permeation through the membrane or by a combination of these two processes (9). The second process is the one desired here and predominates in polymeric materials (30); therefore, further mention will not be made of simple diffusion. Permeation is the process of dissolution of a gas at one surface of the membrane, diffusion through the membrane (analogous to diffusion through a liquid) and evaporation at the other side. In fact, permeation through a polymer film is described mathematically in much the same way as solubility and diffusion in liquids. A mathematical description of permeability will not be given here, but it should be said that temperature has a large effect on permeability in most cases. In some cases such as the permeability of water vapor through polystyrene (21) or carbon dioxide through silicone rubber (18) only a relatively small temperature effect is observed. In general this is more likely to happen with gases that have a high heat of vaporization. Sulfur dioxide is such a gas; therefore, it seemed possible that membranes with little or no temperature permeability effects might be found.

Permeability of a membrane, or the permeability constant as it is

often called, is described by the equation

$$(1) \qquad N = \frac{PA\ (p_1 - p_2)}{s}$$

where N = flow of gas across membrane,

P = permeability,

A = area (cm^2),

s = membrane thickness

and (p_1-p_2) = partial pressure difference across membrane.

This constant is, as was explained earlier, usually temperature dependent. It is obvious from the above equation that the thinner the membrane, the more permeable the membrane becomes. This makes it highly desireable to choose very thin films to promote fast movement of material across the membrane. It was decided, however, not to use membrances thinner than 0.0025 cm (1 mil), since films thinner than this are rather fragile. They may also contain pinholes which allow transmission of gas or liquid.

For convenience, an equation relating the exposure concentration to the amount of sulfur dioxide absorbed will be derived here. Appropriate units are assumed where not specifically indicated. Since the partial pressure of sulfur dioxide on the solution side of the membrane is zero eq. (1) may be rewritten as

$$(2) \qquad N = \frac{PAp_1}{s} .$$

By multiplying both sides of the equation by the time t, we have

(3) $$c = Nt = \frac{PAp_1t}{s},$$

where c (μg/10 ml of solution) is the amount of sulfur dioxide that has penetrated the membrane in time t and been absorbed by the absorbing solution. Since the partial pressure is simply a concentration term, p_1 may be conveniently described by the equation

(4) $$p_1 = aC,$$

where C = concentration of sulfur dioxide in the air (μg/m^3)

and a = constant.

This expression may be substituted into eq. (3) to give

(5) $$c = \frac{PaCAt}{s}.$$

By letting Pa equal the new permeability constant, P_r, we have

(6) $$c = \frac{P_rCAt}{s}.$$

Since P_r, A and s are constants for a given permeation device, eq. (6) may be presented as

(7) $$C = \frac{ck}{t},$$

where $$k = \frac{s}{AP_r}.$$

As can be seen, the concentration of sulfur dioxide in air is proportional to the amount of sulfur dioxide absorbed in the sodium tetra-

chloromercurate (II) solution and inversely proportional to the time of exposure. Therefore, an instrument having a given membrane configuration may be calibrated by exposing it to sulfur dioxide at a known concentration for a given amount of time.

B. INITIAL SCREENING OF MEMBRANES

There is little data available on the permeability of sulfur dioxide (6, 18); therefore, an investigation of this phenomenon was initiated. Various types of membranes were placed in the cell assembly described in Chapter II or on tubes and exposed to sulfur dioxide using duplicate samples of all films except those of teflon. These experiments and the ones dealing with the temperature effect on permeability were carried out with dry air-sulfur dioxide mixtures. This was done to eliminate humidity effects that might occur during changing laboratory conditions and allowed an accurate estimation of the water loss by permeation.

The relative permeabilities of these films are given in Table II. As can be seen, the permeabilities of cellulose acetate, polyethylene, Iolon and the silicone films are the highest. The cellulose acetate film was immediately ruled out because it is very permeable to water vapor. During the exposure period of 16 hours, more than half the water of the absorbing solution was lost. Although the silicone films have much higher permeabilities than the other two, they cannot be heat sealed into a bag. By making the sulfur dioxide measuring device into a bag, a very large area of film can be exposed and a larger amount of sulfur dioxide can permeate through the membrane. Therefore,

TABLE II

PERMEABILITY OF MEMBRANES

Membrane		Exposure			
Type	Source	Time (Hour)	Conc. ($\mu g/m^3$)	Thickness ($cm \times 10^4$)	Relative* Permeability
Cellulose Acetate	Dupont	16.3	11.9	25	2.50
TFE Teflon	Dupont	61.8	11.9	125	0.15
FEP Teflon	Dupont	61.8	11.9	125	0.22
Mylar A	Dupont	68.5	3.7	25	0.17
Poly Vinyl Fluoride	Dupont	68.5	3.8	25	0.61
Iolon	Dupont	39.9	10.5	25	1.02
Polyethylene	Packaging Aids	40.0	10.5	25	1.00
Silastic	Dow-Corning	10.0	3.5	250	389
Dimethyl Silicone (Unbacked)	General Electric	5.0	13.2	25	272
Dimethyl Silicone (Single Backing)	General Electric	0.5	63.1	25	119
Dimethyl Silicone (Double Backing)	General Electric	5.0	13.2	25	310
Silicone-Polycarbonate Copolymer MEM-213	General Electric	0.5	63.1	100	80
Silicone Rubber	Union Carbide	5.0	13.2	100	347

*These permeabilities are measured relative to the permeability of polyethylene which is assumed to be 1.0.

the advantage that the more permeable silicone membranes have is not as great as it may seem simply by consulting the permeability data. There is also the added advantage that the polyethylene and Iolon films are much less expensive and would not need to be reused. Polyethylene and and Iolon films cost less than one cent per square foot. On the other hand, the General Electric silicone films cost as much as twenty to twenty-five dollars per square foot while the M-213 membrane sells for about seven dollars per square foot. On the basis of this information it was decided that the polyethylene, Iolon and silicone rubber films would be examined further. Since the effect of temperature on the permeability of most polymers is quite dramatic, the next step was to examine the effect of temperature on these membranes.

The General Electric single backed film seemed to be an anomaly since it had a much lower permeability than the other silicone films. Later samples, however, proved to be just as permeable as the other silicone films.

Other methods could have been used for determining the permeability, but it seemed desirable to maintain conditions as near as possible to those that would occur during atmospheric analysis. By doing this, long term stability and water loss problems were soon recognized.

C. TEMPERATURE EFFECT

The effect of temperature on the permeability of polyethylene, Iolon and three silicone rubber films can be seen in Figures 7 and 8 and Table III. The Dow-Corning film, which was thicker than the other

FIGURE 7

TEMPERATURE EFFECT ON PERMEABILITY

⊙ Iolon

△ Polyethylene

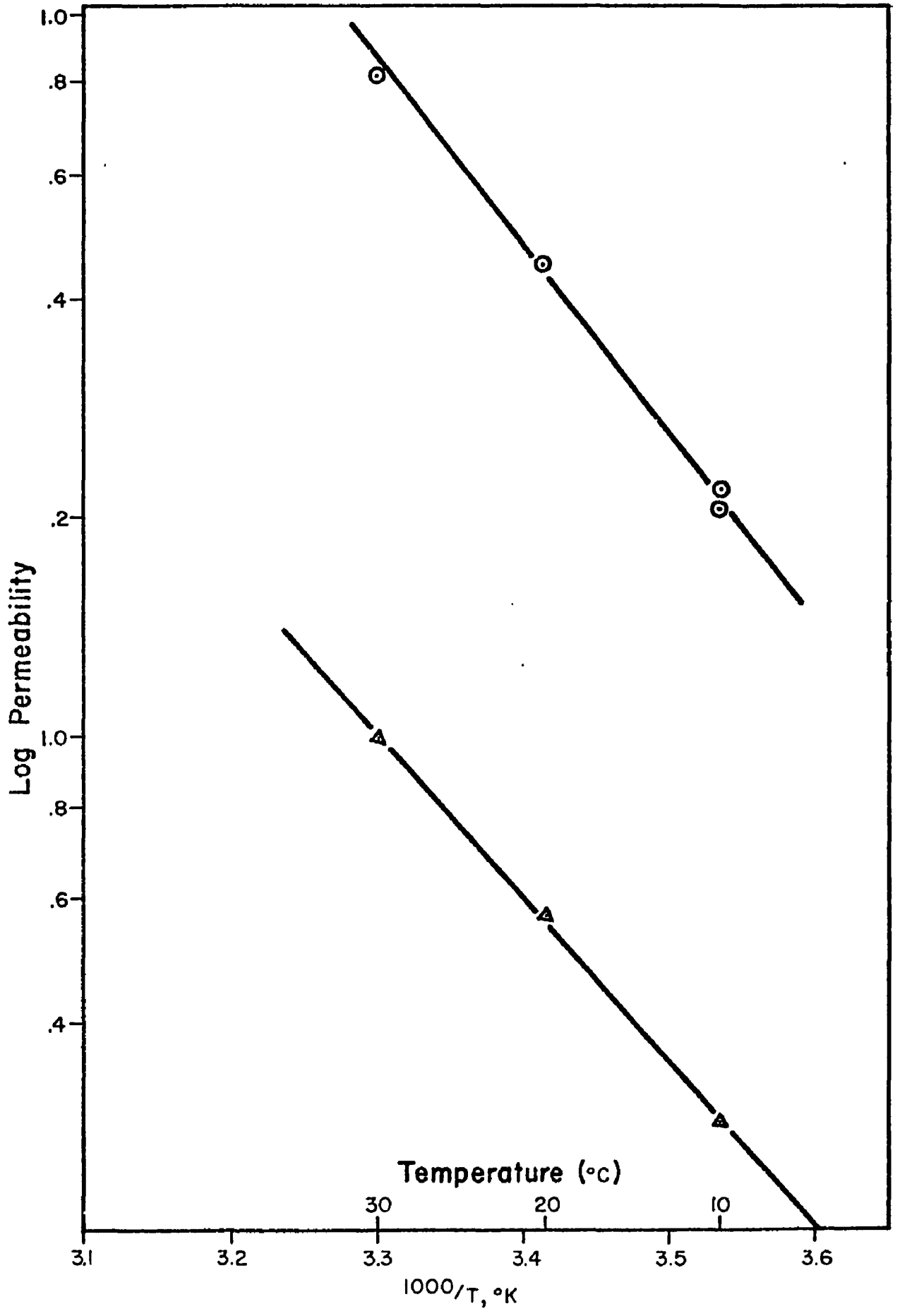

1.0
.8
.6
.4
.2
1.0
.8
.6
.4
Log Permeability
Temperature (°C)
30
20
10
3.1
3.2
3.3
3.4
3.5
3.6
1000/T, °K

FIGURE 8

TEMPERATURE EFFECT ON PERMEABILITY

(Silicone Rubber Films)

⊙ General Electric, Unbacked

△ General Electric, Double Backed

⊡ Union Carbide

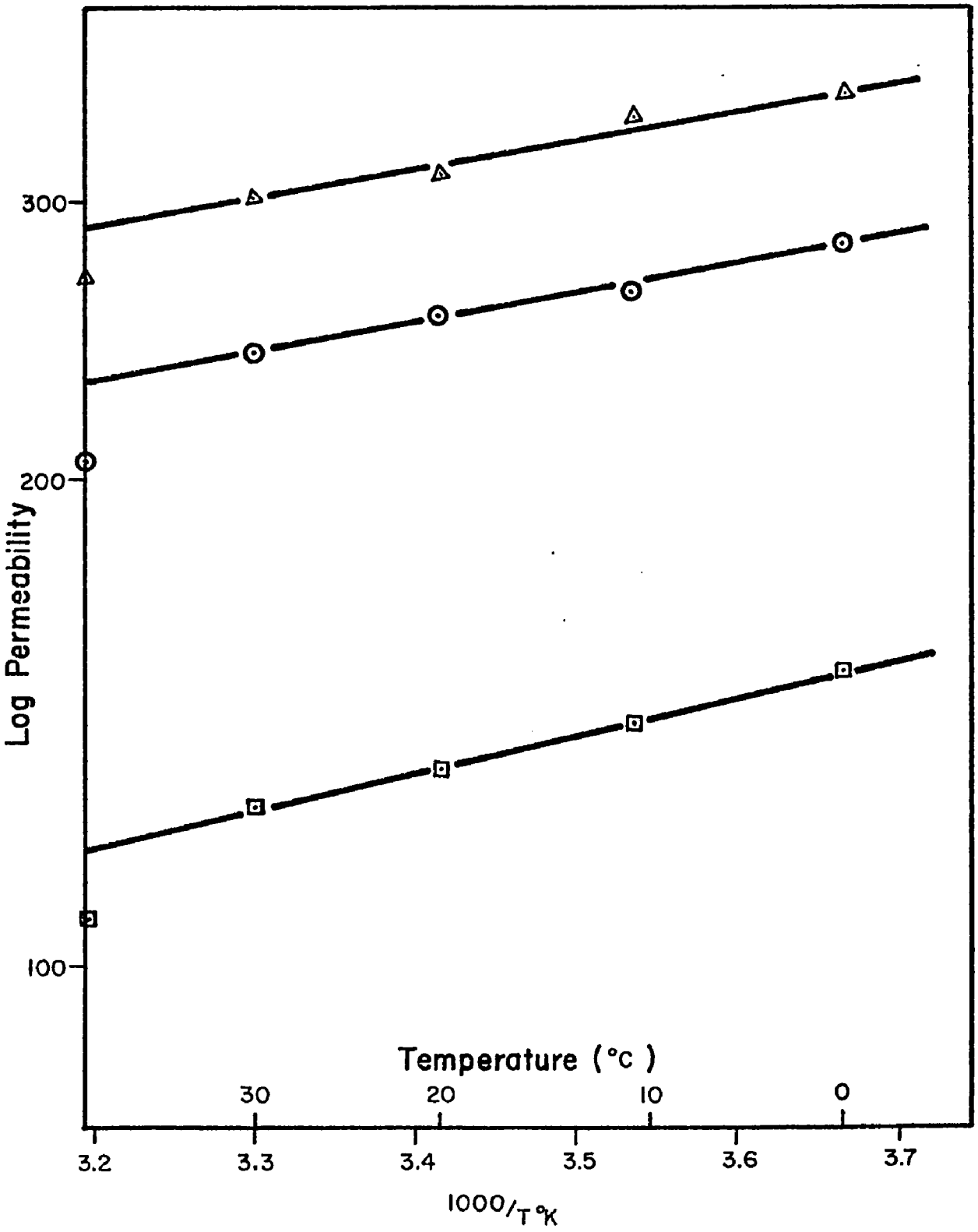

300
200
100
Log Permeability
Temperature (°C)
30
20
10
0
3.2
3.3
3.4
3.5
3.6
3.7
1000/T °K

TABLE III

EFFECT OF TEMPERATURE ON PERMEABILITY

Type and Source	% Error for 10°C Change in Temperature*
Silicone Rubber (Union Carbide)	6.0
Dimethyl Silicone Unbacked (General Electric)	5.2
Dimethyl Silicone Double Backing (General Electric)	4.9
Polyethylene (Packaging Aids Corporation)	109
Iolon (Dupont)	99

*This is the percentage error for an increase in temperature. A decrease in temperature would cause a much smaller error for polyethylene and Iolon. For the silicone films a decrease or an increase in temperature causes almost the same error.

films, was omitted in this and subsequent studies. Here again, permeability is related to polyethylene. Since these plots are logarithmic, neither a simple statement of a certain percentage variation of permeability per °C, nor the slope of the permeability plot would give an accurate measurement of the effect on a device actually used in air pollution work. It might seem reasonable to use the percentage variation of the logarithm of the permeability, but this figure must always be converted to percentage variation of permeability which is the quantity that will be observed in actual use. It was decided, therefore, to represent this data on the basis of what would happen during a normal or average exposure in the atmosphere for a period of several days, assuming that during a normal exposure, the temperature would vary ± 10°C from the mean. Therefore, the percentage variation of permeability for a 10°C change in temperature is used as the method for representing the temperature effect. This data is given in Table III.

The polyethylene and Iolon films have a permeability change of about 100% for a 10°C change in temperature, while the three silicone rubber films have a permeability change of about 5% per 10°C. This indicates that the silicone membranes are far superior where anything but very small variations in temperature are encountered. At this point it was obvious that only silicone rubber films would work satisfactorily as a membrane for the sulfur dioxide measuring device. Since the General Electric membranes were thinner than the other silicone films and more sulfur dioxide could permeate them at a given

concentration, it was decided to use them in the rest of these studies.

D. HUMIDITY EFFECT ON MEMBRANE PERMEABILITY

Permeability is in many cases a very humidity dependent phenomenon (21); however, the sulfur dioxide permeability of the silicone rubber membranes tested here was relatively independent of humidity. It can be seen in Table III that the permeability does not vary at the relative humidities of 0% and 80%.

TABLE IV

EFFECT OF RELATIVE HUMIDITY ON
PERMEABILITY OF SULFUR DIOXIDE

Type	0%	80%	80% w/condensation
Unbacked	0.201	0.196	0.192
Single backed	0.205	0.202	0.204
Double backed	0.160	0.165	0.171

A third study was made with the 80% relative humidity air-sulfur dioxide mixtures by adding chilled sodium tetrachloromercurate (II) solution to the tubes instead of room temperature solution. This caused condensation on the tubes which stayed present for about 1.5 hours out of the 5-hour exposure period. This study was designed to indicate what would happen if dew formed on the membrane when the permeation device was exposed to the ambient atmosphere. It was expected that the water coating the membrane might allow oxidation of

the sulfur dioxide before permeation could occur or act as a barrier to the sulfur dioxide. As can be seen in Table IV even with condensation, no change in the permeability occurred. This indicates that the sulfur dioxide in the air saturates the water on the surface; then the sulfur dioxide continues on its path through the membrane. The term saturate here means to saturate at the given sulfur dioxide partial pressure that the permeation device is being exposed to. Since at saturation the sulfur dioxide in the water has a partial pressure equal to that of the sulfur dioxide-air mixture, the partial pressure that the membrane experiences (the partial pressure of sulfur dioxide in the water) is equal to that of the air. Therefore, the water layer has no effect on permeation. If oxidation had occurred at a rate comparable to the rate that the sulfur dioxide was absorbed by the water, then there would have been a reduction in the experimental permeation rate. This situation could still possibly occur in the ambient atmosphere if metal catalysts that would increase the rate of oxidation of sulfur dioxide were absorbed in the condensed water.

E. RESPONSE TIME

Permeation through polymer films is not an instantaneous phenomenon. In fact, in some cases, it takes several hours or even days for a gas to penetrate a membrane. The time between the initial exposure of one side of a membrane to a gas and the start of emission of the gas from the other side is called the time lag. It is important to characterize this phenomenon in the present studies so that the response of the final sulfur dioxide measuring instrument to short

term exposures can be predicted. The term time lag, which helps describe permeation mathematically, may be replaced here by the similar term response time which is more convenient from an analytical chemist's point of view. Fortunately, the response time is very short as shown in Fig. 9. In fact, the amount of sulfur dioxide absorbed during the first 10 minute period is almost 90% of the steady state value. This actually means that the permeation rate reaches 90% at some time shorter than 10 minutes. A good estimate would probably be 2 to 3 minutes since the rate of permeation in most polymers will remain near zero for the time lag period, then abruptly increase. Shorter time periods than 10 minutes could not be examined with the present equipment.

F. STABILITY OF SULFUR DIOXIDE IN SODIUM TETRACHLOROMERCURATE (II) SOLUTIONS

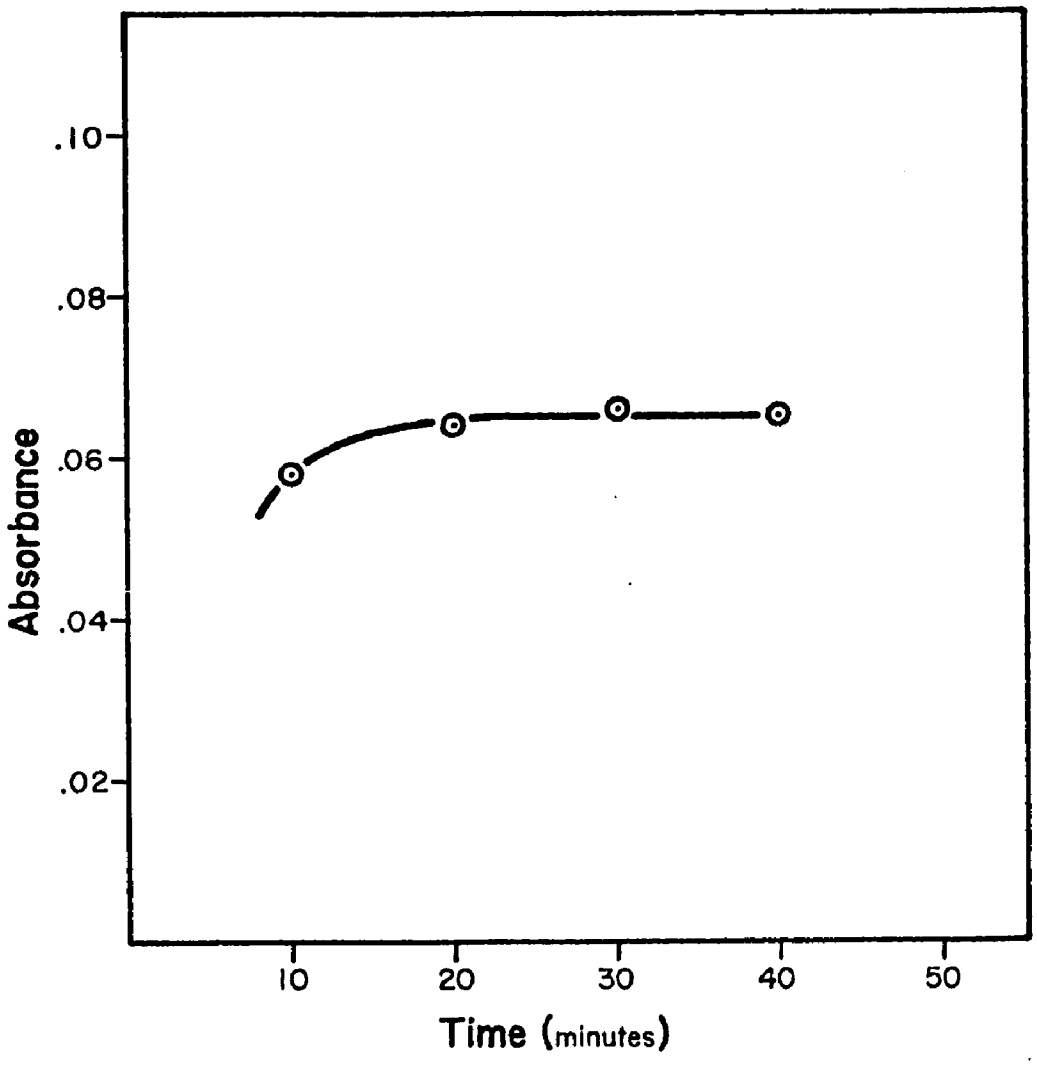
Sulfur dioxide is stabilized in sodium tetrachloromercurate (II) solutions as the very stable dichlorosufitomercurate (II) complex (23). The sulfur dioxide in this complex resists oxidation, even by permanganate.

Solutions of tetrachloromercurate (II) were charged with gaseous sulfur dioxide rather than the usual sulfite since it was convenient to add sulfur dioxide with the sulfur dioxide-air mixture preparation apparatus. The stability of sulfur dioxide in tetrachloromercurate (II) solutions has been measured (25, 26, 27, 28, & 29), but only a few examinations of the effect of temperaure (25 & 28) and concentration of tetrachloromercurate (II) (25) on the stability of sulfur di-

FIGURE 9

RESPONSE TIME

(Dimethyl Silicone, General Electric)


.10
.08
.06
.04
.02
Absorbance
10
20
30
40
50
Time (minutes)

oxide have been completed. It was, therefore, deemed necessary in the present study that a thorough investigation of the stability of sulfur dioxide in tetrachloromercurate (II) solutions be initiated. A major objective of this investigation was to enhance the stability of sulfur dioxide in solution.

The stability of sulfur dioxide in the absorbing solution was studied by maintaining sulfur dioxide containing sodium tetrachloromercurate (II) solutions at a constant temperature. A sulfur dioxide-air mixture from the permeation apparatus was bubbled through the various sodium tetrachloromercurate (II) absorbing solutions to obtain a given concentration of sulfur dioxide. These solutions were then placed in polyethylene bottles and the bottles were in turn placed in a constant temperature bath. Over a period of several days or several weeks, aliquots of 10 ml were withdrawn periodically and analyzed for sulfur dioxide by the procedure in Chapter II, Section B. Scaringelli, et. al. (26) indicated that the sulfur dioxide oxidation reaction is first order and that it follows the equation

$$\ln C = kt + \ln C_o,$$

where $\ln C$ = natural log of observed concentration,

k = rate constant,

t = elapsed time

and $\ln C_o$ = natural log of concentration at time zero.

Present studies also confirm this first order reaction plot. Plots representative of these studies are shown for 0.1 M and 1 M sodium

FIGURE 10

STABILITY OF SULFUR DIOXIDE IN 0.1 M

SODIUM TETRACHLOROMERCURATE (II)

⊙ 30°C

△ 40°C

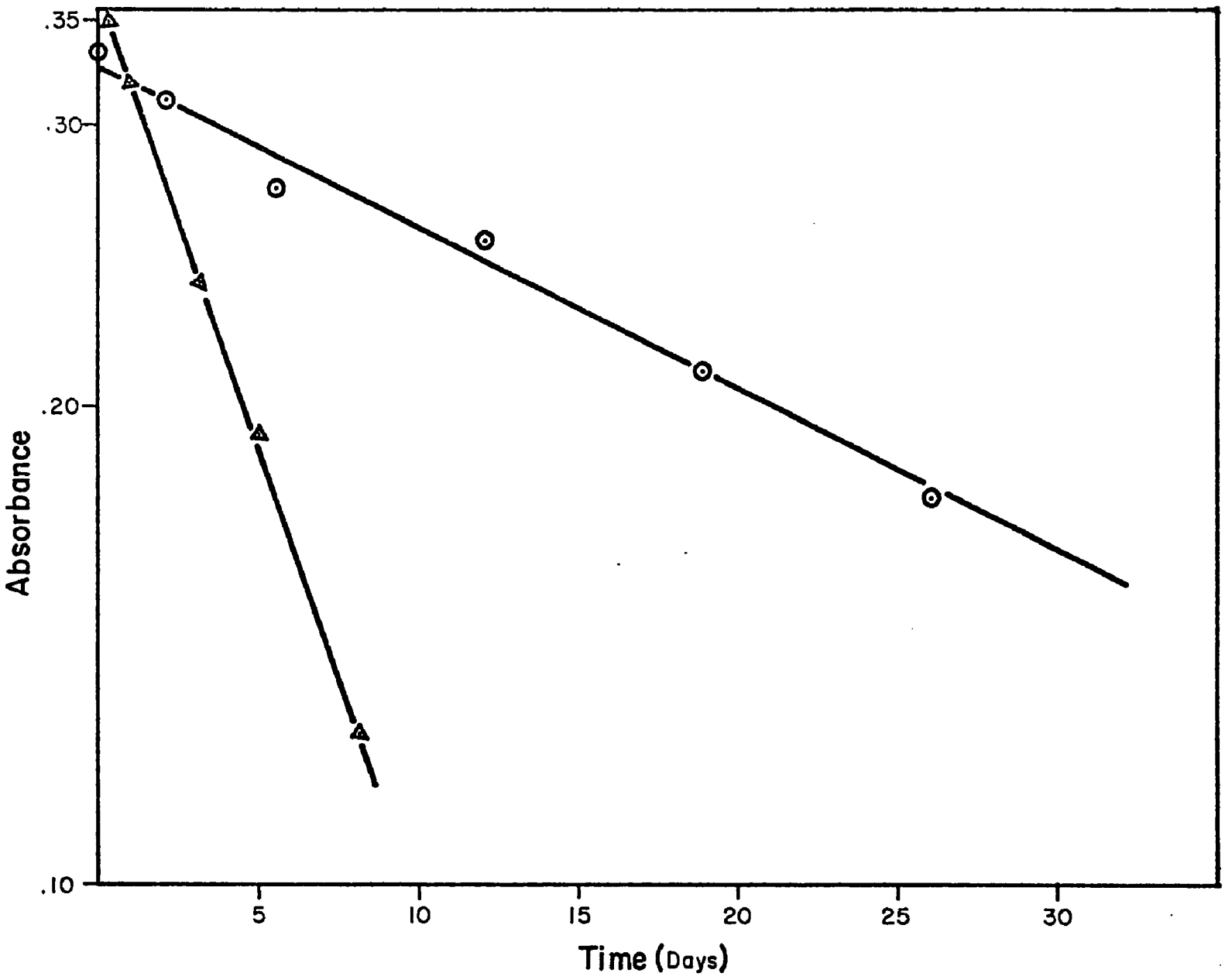

.35
.30
.20
.10
Absorbance
5
10
15
20
25
30
Time (Days)

FIGURE 11

STABILITY OF SULFUR DIOXIDE IN 1 M

SODIUM TETRACHLOROMERCURATE (II)

⊙ 40°C

△ 30°C

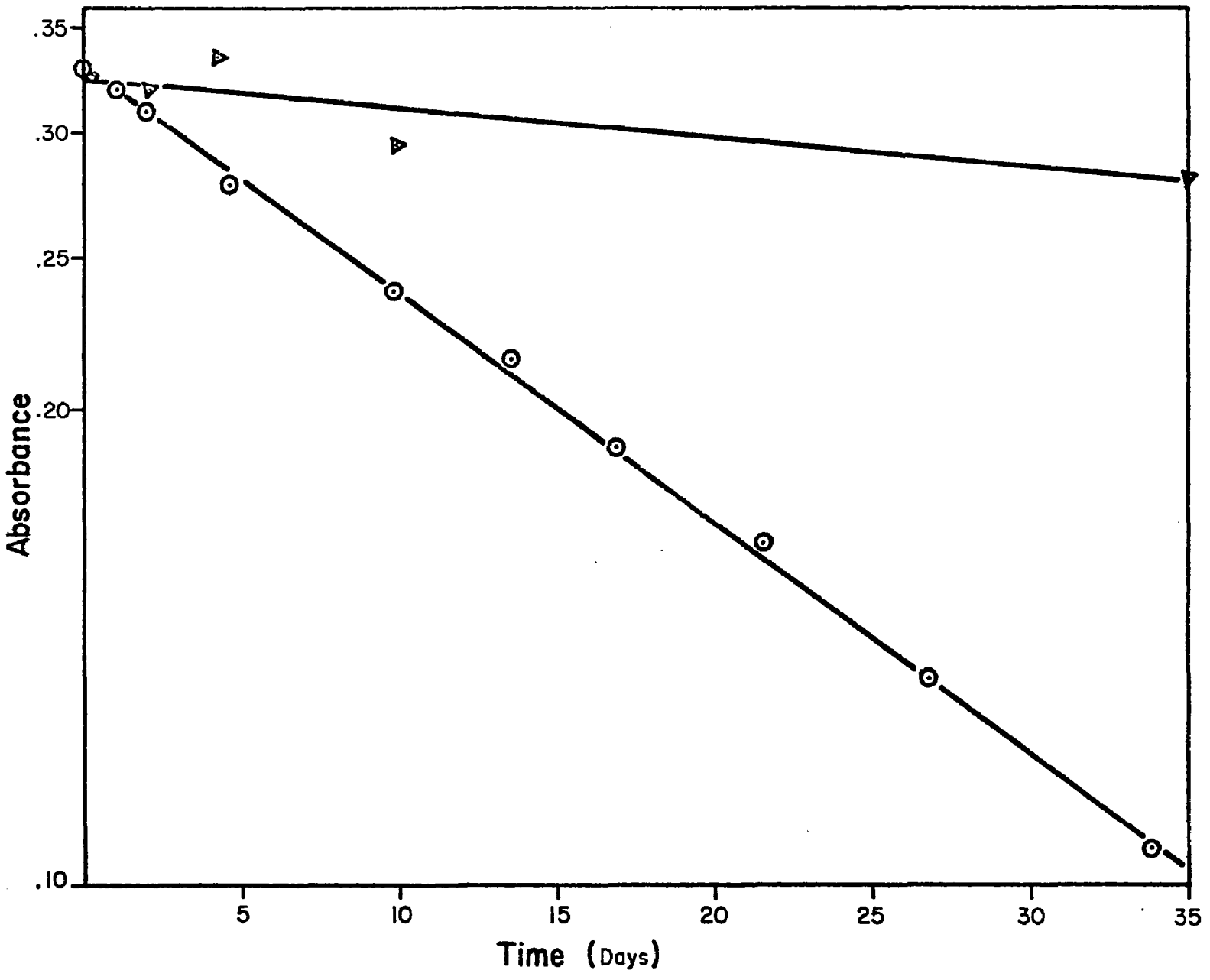

.35
.30
.25
.20
.10
Absorbance
5
10
15
20
25
30
35
Time (Days)

TABLE V

STABILITY OF SULFUR DIOXIDE IN

TETRACHLOROMERCURATE (II) SOLUTION

Concentration (M)	Temperature (°C)	% Decay (Per 10 Days)	% Decay (Per Day)
.1	30	21	2.5
.1 EDTA	30	22	2.7
.1	40	74	12
.1*	40	73	12
.4	40	42	5.2
1	30	4	0.5
1	40	28	3.0
1**	40	27	2.8
1 EDTA	40	29	3.7

*This solution was made with potassium chloride instead of sodium chloride.

**The starting concentration of sulfur dioxide in this solution was 2 µg/ml rather than 1 µg/ml as in the others.

tetrachloromercurate (II) solutions in Figs. 10 & 11. Other data are presented in Table V. The percentage of sulfur dioxide oxidized during one and ten day periods is given rather than the slope of the decay curves so that a better understanding of the relationships between decay and time can be obtained. Scaringelli also indicated that faster decay of sulfur dioxide occurred if the solutions were charged with more than 0.2 µg/ml sulfur dioxide unless disodium ethylenediaminetetraacetate (EDTA) was also added to the tetrachloromercurate (II) solution. The data given here show this not to be the case with 0.1 M and 1 M sodium tetrachloromercurate (II) solutions; however, Scarengelli used 0.04 M potassium tetrachloromercurate (II) solutions. He also made sulfite rather than gaseous sulfur dioxide additions. Further, it can be seen by comparing the 40°C studies that sulfur dioxide is more stable in the stronger tetrachloromercurate (II) solutions. Undoubtedly, stronger solutions than 1 M would result in further decrease in the decay rate of sulfur dioxide. Because of the gross amounts of mercuric chloride that were necessary even for 1 M solutions, it was decided not to pursue this route further and to use 1 M solutions in subsequent studies. A calibration curve using this solution is given in Figs. 12 and 13.

The curve is linear up to about 8 µg sulfur dioxide per 10 ml, but deviates from linearity at higher concentrations. The absorbance maximum occurs at 575 nm and color development reaches a maximum 40 minutes after addition of reagents.

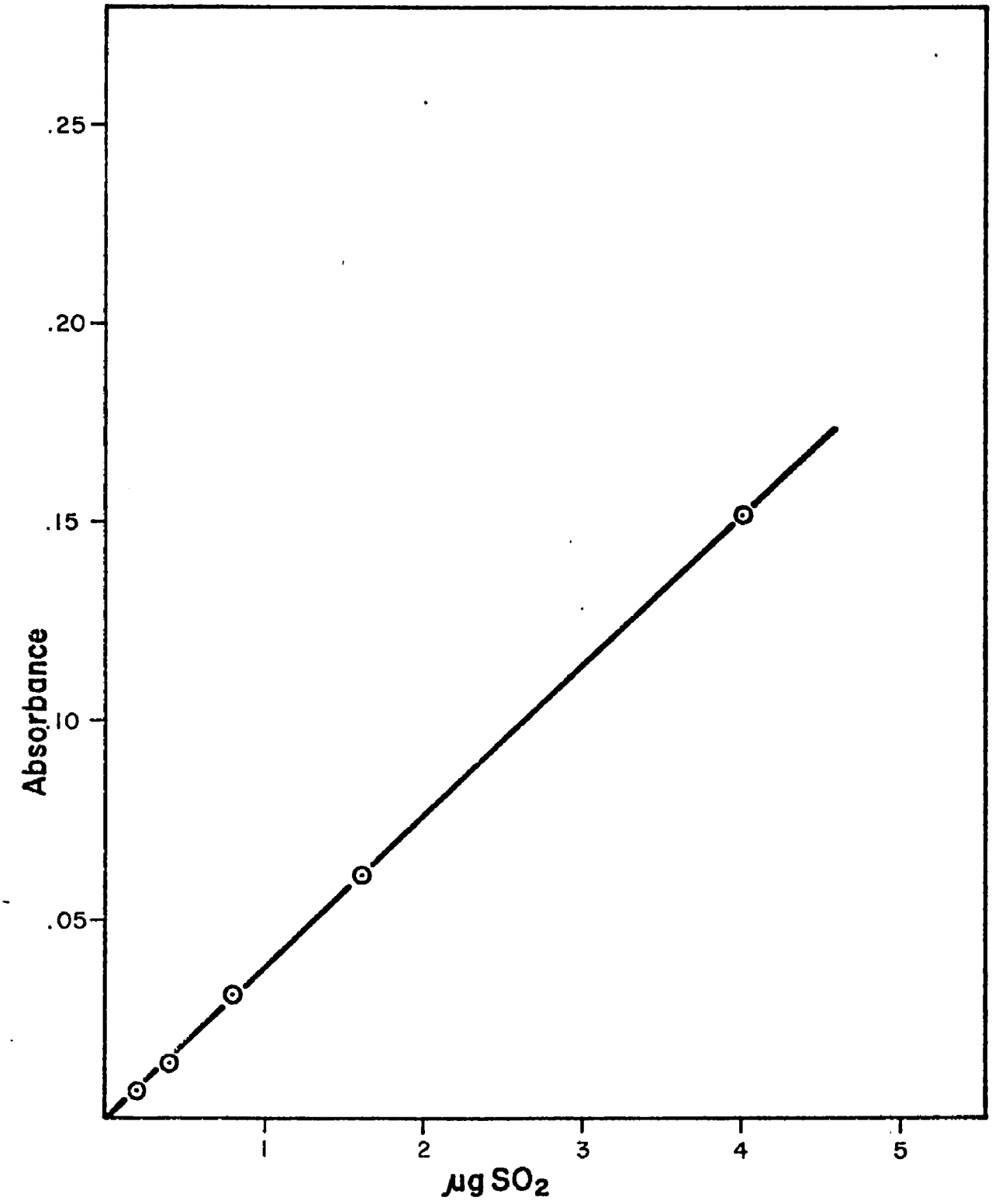
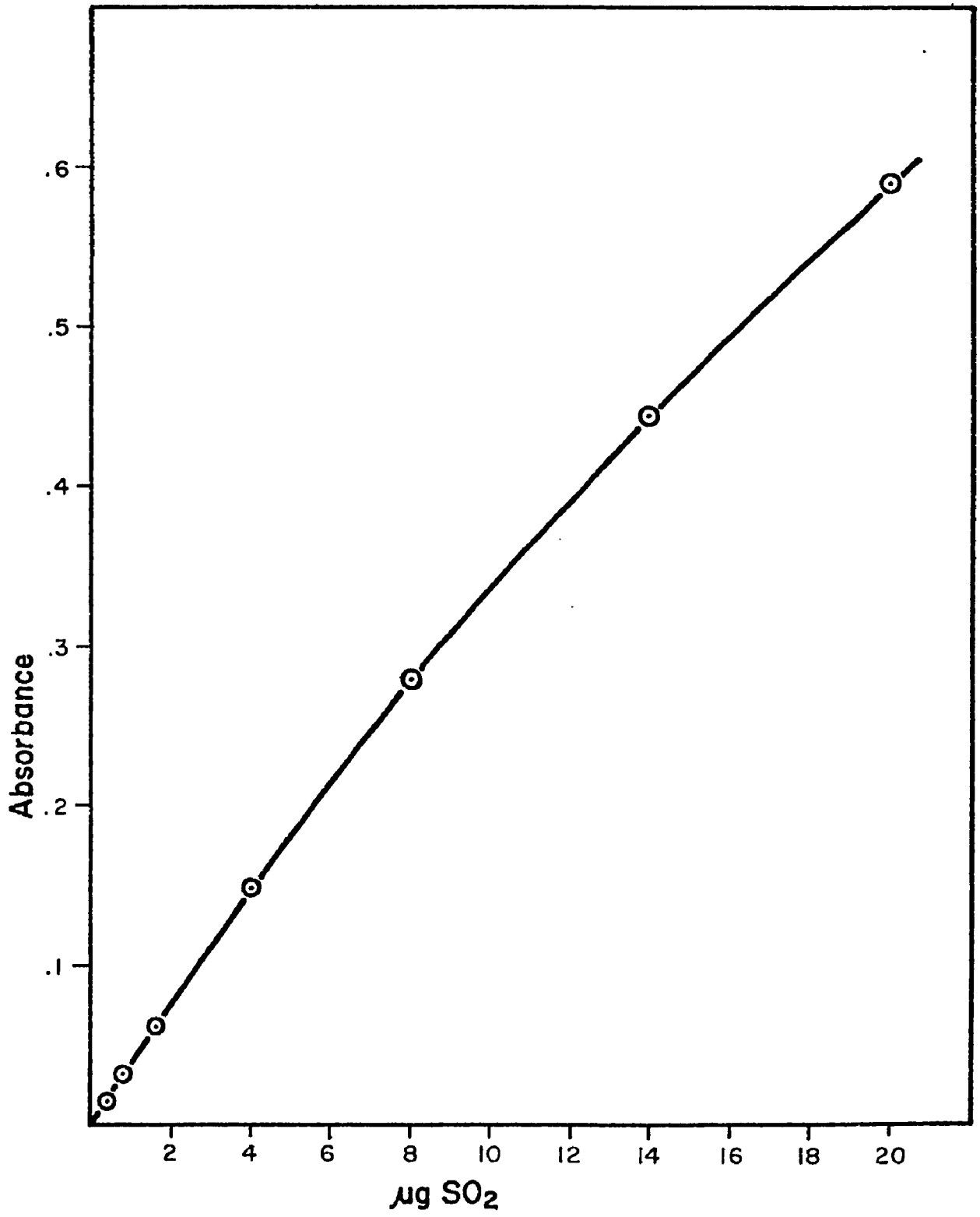

.25
.20
.15
.10
.05
Absorbance
1
2
3
4
5
µg SO2

FIGURE 13

CALIBRATION CURVE FOR SULFUR DIOXIDE

IN 1 M SODIUM TETRACHLOROMERCURATE (II)

Range: 0 - 20 μg


.6
.5
.4
.3
.2
.1
Absorbance
2
4
6
8
10
12
14
16
18
20
µg SO2

G. INTERFERENCE STUDIES

A description of the procedures used for the interference studies is given in Chapter II. The main purpose of these experiments was to investigate the effect of hydrogen sulfide, ozone and nitrogen dioxide on the final form of the sulfur dioxide measuring instrument taking into consideration the fact that it may be exposed to the foreign gas before, during or after exposure to sulfur dioxide. It seemed reasonable to relate the concentration of the possible interfering gas to the appropriate Federal or State standards (31, 35).

There are no Federal standards for hydrogen sulfide concentrations; nevertheless, Texas has recently set a maximum permissible concentration of 15 $\mu g/m^3$ (24 hour average) (35). A concentration of 600 $\mu g/m^3$ or 4,500 $\mu g/m^3$ or 20 and 300 times this standard was used here for a period of 20 hours. Under these rather harsh conditions, experimental errors less than 10% (Table VI) were found in all cases. However, the tubes exposed to 4,500 $\mu g/m^3$ hydrogen sulfide developed pinhole leaks in the membrane. The membranes also turned light brown during the experiments. The membranes that developed pinholes also were observed to have bright yellow spots. Undoubtedly the hydrogen sulfide being absorbed was decomposed to give sulfur or precipitated as mercuric sulfide.

The Federal Standard for ozone (photochemical oxidants) is 170 $\mu g/m^3$ for a 1 hour exposure. A 1 hour exposure to 500 $\mu g/m3$ or 3 times the standard was used here. The results of these experiments are given in Table VII. Losses of sulfur dioxide ranged to as high

TABLE VI

INTERFERENCE OF HYDROGEN SULFIDE

Tube No.	Absorbance		
	Calculated	Measured	Error
Exposed to sulfur dioxide * then to hydrogen sulfide:**			
1	0.112	0.113	0.001
2	0.218	0.211	-0.007
33	0.372	0.382	0.010
Exposed to hydrogen sulfide then to sulfur dioxide:			
12	0.112	0.120	0.008
20	0.132	0.130	-0.002
Exposed to mixture to sulfur dioxide and hydrogen sulfide:			
12	0.260	0.235	-0.025
20	0.307	0.292	-0.015

*The absorbing solutions had been charged with sulfur dioxide prior to exposure to hydrogen sulfide.

**These tubes were exposed to 4,500 $\mu g/m^3$ rather than the 600 $\mu g/m^3$ of hydrogen sulfide used in the other experiments in this series.

TABLE VII

INTERFERENCE OF OZONE

Tube No.	Absorbance		
	Calculated	Measured	Error
Exposed to sulfur dioxide* then to ozone:			
13	0.075	0.059	-0.016
14	0.146	0.142	-0.004
18	0.281	0.265	-0.016
Exposed to ozone then to sulfur dioxide:			
13	0.113	0.092	-0.021
14	0.111	0.100	-0.011
18	0.143	0.116	-0.027
Exposed to ozone and sulfur dioxide simultaneously:			
13	0.108	0.097	-0.009
14	0.107	0.094	-0.013
13	0.095	0.095	0.000
14	0.094	0.088	-0.006

*The absorbing solutions were charged with sulfur dioxide prior to exposure to ozone.

as 0.8 μg (20% error) with an average loss of 0.3 μg (10% error).

The present Federal standard for maximum permissible nitrogen dioxide is 100 $\mu g/m^3$ (1 year mean). No standard for a shorter time period exists. A 24 hour standard would probably be about three times this large; therefore, the concentration used here of 1400 $\mu g/m^3$ would be roughly 5 times a 24 hour standard if there were one. The results shown in Table VIII indicate that the use of sulfamic acid is essential when nitrogen dioxide is present at these concentrations. This does cause serious (50%) suppression of the color development. It should also be noticed that the error due to nitrogen dioxide was almost negligible if the tube was exposed to sulfur dioxide before exposure to nitrogen dioxide. Exposure to nitrogen dioxide before sulfur dioxide exposure or simultaneously with sulfur dioxide caused fairly large interferences from 5-30% error. In all cases throughout this interference study as is typical of the West-Gaeke method, only negative interferences were observed.

H. FINAL FORM OF THE PERMEATION DEVICE

Protection of the absorbing reagent from contaminated air is not difficult in the laboratory since the open end of the permeation device is not exposed to contaminated air, but in the ambient atmosphere this is not the case. The tube may be stoppered to prevent free movement of air in and out of the tube, but this will strain the membrane when the air inside the tube is heated or cooled. Therefore, a glass capillary is inserted through the stopper. This allows free movement of the small amounts of air needed to equilibrate the pressure

TABLE VIII

INTERFERENCE OF NITROGEN DIOXIDE

Tube No.	Absorbance			Sulfamic Acid Added
	Calculated	Measured	Error	
Exposed to sulfur dioxide* then to nitrogen dioxide:				
13	0.148	0.151	0.003	yes
14	0.068	0.069	0.001	yes
15	0.033	0.030	-0.003	yes
13	0.274	0.169	-0.105	no
14	0.059	0.029	-0.030	no
15	0.059	0.028	-0.031	no
Exposed to nitrogen dioxide then to sulfur dioxide:				
13	0.266	0.085	-0.181	no
14	0.161	0.150	-0.011	yes
18	0.208	0.175	-0.033	yes
Exposed to a mixture of nitrogen dioxide** and sulfur dioxide:				
13	0.173	0.082	-0.091	no
14	0.085	0.065	-0.020	yes
15	0.109	0.077	-0.032	yes

*The absorbing solution was charged with sulfur dioxide prior to exposure to nitrogen dioxide.

**The concentration of nitrogen dioxide was 700 $\mu g/m^3$ for this experiment.

across the membrane. No measurable leakage of sulfur dioxide is found even at 5,000 $\mu g/m^3$ for a 24 hour exposure.

The permeation instrument must also be protected from direct sunlight since intense light causes oxidation of sulfur dioxide to occur (25). A shelter that will allow free movement of air but will eliminate sunlight is in order.

I. INFLUENCE OF SULFUR DIOXIDE CONCENTRATION ON THE PERMEABILITY CONSTANT

One might amply ask at this point if the permeability constant is really constant. In many cases, such as the permeation of water vapor through cellulose acetate, permeability is not constant. Generally, it does remain constant at low concentrations of the permeating species such as those observed in ambient air. It must be understood that the term low concentration used here may be considered a high concentration when related to air pollution.

Confirmation that permeability is truly constant is given in Table IX. It can be seen that permeability varies by less than 8% over the 60-fold range of these experiments. This is probably within experimental error.

J. PRECAUTIONS FOR HANDLING SODIUM TETRACHLOROMERCURATE (II) SOLUTIONS

Finally, it must be remembered that mercury is a very toxic material. Mercury-containing solutions should not be allowed to come in contact with skin. The absorbing solution used here is particularly dangerous since it contains a high concentration of mercury. Also the

sodium tetrachloromercurate (II) solution constitutes a potential pollution hazard in itself. Therefore, it is inadvisible to discharge this mineral waste into a sewer system after analysis. A recent paper has indicated that inorganic mercury may be precipitated as mercuric sulfide and sent to mercury reclamation centers for recycling (4).

TABLE IX

DEPENDENCE OF PERMEABILITY ON

CONCENTRATION OF SULFUR DIOXIDE

Concentration of Sulfur Dioxide ($\mu g/m^3$)	----------k* x 10^{-3}---------- ($\mu g^{**}/m^3$ hr μg^{***})	
	Tube No. 11	Tube No. 16
3,550	1.00	1.25
568	.96	1.16
62	1.01	1.19

*This constant is inversely proportional to permeability and is dependent on film thickness and area. These last two parameters are constant for each permeation device.

**This is µg relative to the concentration of sulfur dioxide in air.

***This is µg of sulfur dioxide absorbed in the absorbing solution.

CHAPTER IV

RECOMMENDED PROCEDURE

A. PREPARATION OF THE PERMEATION DEVICE

Prepare the permeation device as in the experimental section with the following addition. Place a 10 cm length of 1 mm glass heavy wall capillary into a one hole rubber stopper, then place the stopper into the open end of the permeation device. Glass tubing up to 45 mm O. D. can be used. For a 1 day exposure period a 41 mm O. D. (37 mm I. D.) tube 8 cm long is satisfactory.

B. CALIBRATION

Place 10 ml of 0.1 or 1 M sodium tetrachloromercurate (II) in the permeation device. Expose to a known concentration of sulfur dioxide for an appropriate time--typically 3,000 $\mu g/m^3$ for 2 hours--making sure that less than 2% of the sulfur dioxide in the calibration mixture is absorbed by the permeation instruments being exposed. Larger losses of sulfur dioxide can be tolerated by sacrificing calibration accuracy. The constant k is then calculated from a rearrangement of eq. 7:

$$k = \frac{Ct}{c}, \tag{8}$$

where k = constant,

C = concentration of sulfur dioxide ($\mu g/m^3$),

t = time (hours)

and c = amount sulfur dioxide absorbed (μg).

and formaldehyde solutions. Read the absorbance at 575 nm after 40 minutes and find the total μg of sulfur dioxide in the solution from a calibration plot. Calculate the average concentration of sulfur dioxide in air from eq. 7;

$$C = \frac{ck}{t}. \tag{7}$$

To calculate C, the usual standard conditions of 760 mm of mercury and 25°C, k may be multiplied by the factor given in the calibration section using the average temperature and pressure during the exposure.

CHAPTER V

CONCLUSIONS

The method developed here is both sensitive and selective. It definitely is superior to the lead candle method. No pumps, electrical connections, flowmeters or flow regulators need to be used; however, several precautions must be taken to ensure reliable results:

a. An adequate shelter must be used to eliminate light.
b. Sulfamic acid should be used when nitrogen oxides are suspected.
c. The permeation device should not be used at sustained temperatures above 40°C nor at temperatures below -6°C.

The highest temperature that the device is exposed to can be obtained conveniently by placing an ordinary body thermometer near the permeation device. A detection limit of about 10 $\mu g/m^3$ can be stated assuming the detection limit to be twice the blank of 0.008 absorbance units. Present studies indicate the blank varies by less than ± 0.002. An error of less than 10% occurs for a 24 hour exposure at 60 $\mu g/m^3$ under laboratory conditions. A more thorough error analysis will not be given since varying field conditions (temperature, interferences, etc.) may cause errors far different from those that would be obtained from statistical calculations.

Additional investigation of the sodium tetrachloromercuate (II) absorbing solution would be appropriate for future work. It is entirely

possibly that changes in the absorbing solution could affect an increase in sulfur dioxide stability thereby allowing the use of the device at higher ambient temperatures. An antifreeze would allow use at temperatures below -6°C.

Using permeability as a method for controlling sampling rate could undoubtedly be applied to other air or even water sampling systems. It is entirely possible that permeation methods for sampling nitrogen dioxide, hydrogen sulfide, ozone and other gaseous pollutants can be developed.

An appropriate extension of the present work would include the use of sodium hydroxide as the absorbing solution. Sulfur dioxide could then be oxidized to sulfate and be determined turbidimetrically or nephelometrically. At first thought this might be considered a step backwards; however, this would eliminate almost all interferences except hydrogen sulfide, there would be no need to stabilize sulfur dioxide and excessive amounts of light and heat would have no ill effects. Long term samples would be appropriate since sensitivity would be decreased. Besides, this would give the 3 month lead candle people something to switch to!

A further extension might include the use of silicone membranes in stack sampling. Inert gases or absorbing solutions could be used on the sample side of the permeation device.

The applications of permeation mentioned here are not exhaustive but are given only as examples of further use. Very little work has been done with permeation in air pollution studies and the future of the method looks promising.

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EXAMINATION AND THESIS REPORT

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